PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : D06M 13/236, 13/203, 13/222 // 101:32, A01N 25/10, 25/34

A1

(11) International Publication Number: **WO 98/03718**

(43) International Publication Date: 29 January 1998 (29.01.98)

(21) International Application Number: PCT/NZ97/00094

(22) International Filing Date: 24 July 1997 (24.07.97)

(30) Priority Data:
299051 24 July 1996 (24.07.96) NZ

(71) Applicant *(for all designated States except US)*: WOOL RESEARCH ORGANISATION OF NEW ZEALAND INC. [NZ/NZ]; Corner of Gerald Street and Springs Road, Lincoln, Canterbury (NZ).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: LEFTLY, Steven, Andrew [NZ/NZ]; Flat 1, 505 New Brighton Road, Christchurch (NZ). INGHAM, Peter, Edward [NZ/NZ]; 282 Kennedys Bush Road, Halswell, Christchurch (NZ). KING, Cynthia, Kathleen [NZ/NZ]; 259 Spark Road, Christchurch 8002 (NZ).

(74) Agents: LYTH, Richard, John et al.; Baldwin Son & Carey, 342 Lambton Quay, Wellington (NZ).

(81) Designated States: AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), EE, EE (Utility model), ES, FI, FI (Utility model), GB, GE, GH, HU, IL, IS, JP, KE, KG, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
With international search report.
With amended claims.

(54) Title: A METHOD FOR INSECT-RESIST TREATMENT OF CARPETS, TEXTILES AND INSULATION PRODUCTS

(57) Abstract

A method of insect-resist treating carpets, textiles and insulation products and a product produced by the method in which a proportion of synthetic or regenerated natural fibre, which has been pre-treated with an effective insecticide, is blended with wool fibres. The effective insecticide can be any insect growth regulator which has an insect-resist effect such as permethrin. When using the pre-treated fibre to insect-resist wool the aim is to add as little as possible to the overall fibre blend so as to minimise the proportion of synthetic or regenerated natural fibres in the blend.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

A METHOD FOR INSECT-RESIST TREATMENT OF CARPETS, TEXTILES AND INSULATION PRODUCTS

BACKGROUND

This invention involves a method of imparting insect-resistance on carpets, textiles or insulation products which contain wool and/or other animal fibres.

All goods containing wool and other animal fibre components are susceptible to damage caused by insects. Presently these fibre components are treated with insecticides to render them resistant to insect attack.

The most common insecticides used to give wool fibres insect resistance are synthetic pyrethroids, usually permethrin. These are usually applied by adding an aqueous emulsion of the insecticide to wool during scouring, dyeing, tape-scouring or chemical-setting.

The insecticide active is exhausted into and onto the fibres in the above applications. In the case of dyebath application typically 95% of the insecticide is exhausted onto the fibre. With loose wool or yarn scouring application processes, a continuous exhaustion equilibrium is reached being partially dependent on fibre throughput and bowl insecticide concentration. In both the above application processes considerable amounts of effluent containing insecticide are produced.

These effluents are environmentally undesirable in that they may have adverse effects on aquatic organism populations in waters to which the

effluent is eventually discharged (usually via sewerage or other waste treatment). This may have an adverse effect on other species down the food chain.

In some geographic areas strict limits are being imposed on the discharge of effluent containing these insecticides. These limits can be such that traditional insect-resist treatment methods as described above, cannot be used if effluent is discharged directly to sewer.

The purpose and object of this invention is to overcome the problems of pesticides present in discharge effluents i.e. to produce an alternative to traditional aqueous application methods.

SUMMARY OF THE INVENTION

The nature of the invention is to blend a proportion of synthetic or regenerated natural fibre, which has been pre-treated with an effective insecticide, with wool fibres.

The effective insecticide can be permethrin, an insect growth regulator or any other compound having an insect-resist effect.

The insect growth regulator can be RH 5992 (Rohm & Hass) and the insect-resist compound can be Abamectin, Lufenuron (Ciba Geigy), Bifenthrin (FMC Corporation), MGK 264 or a perfluoroalkylsulphonate (3M).

When using the pre-treated fibre to insect-resist wool the aim is to add as little as possible to the overall fibre blend so as to minimise the proportion of synthetic or regenerated natural fibres in the blend.

This could be, for example, <5% synthetic fibre of overall weight of wool. Because wool eating insects do not selectively graze wool fibres the pre-treated component effectively protects the whole fibre blend.

A secondary but very important feature of the invention is for the pre-treated fibre to contain a high concentration of insecticide (for example permethrin) to impart insect resistance on the whole fibre blend. The choice of fibre for treatment and the method of insecticide application to the fibre are key features of the invention. Another key factor is that the insecticide treatment is largely fast to subsequent wet processes. This is essential to prevent downstream losses of the insecticide which end up in discharged effluent.

DESCRIPTION OF PREFERRED EMBODIMENTS

The process of application and its inherent properties will be apparent from the following examples.

Example 1

Low-melt bi-component polyester fibre (PES) (LM-51, 15 den, 76 mm - SAM YANG Co Limited) was pre-treated in a bath containing 1 g/l Topsoft (Dylachem - Precision Processors) for 15 minutes at 40°C.

The fibre is then squeezed and added to the application bath which contains:

- 30% owf Mystox CMP (Catomance) (containing 12%

permethrin W/V)

- 10% owf Dyapol BLF (Yorkshire Chemicals)
- pH 4.5 with acetic acid (BDH).

The bath temperature is raised to 55°C and held for 60 minutes.

Fibre is then squeezed and rinsed twice in 40°C rinsewater. The fibre generally takes up about 15% Mystox CMP on weight fibre (owf) (i.e. 1.8% w/w permethrin owf). The dry fibre was blended with wool in the ratio (95% wool/5% PES) to achieve an overall treatment level of about 0.75% Mystox CMP owf (i.e. 0.09% w/w permethrin owf).

The fibre was spun into yarn and then tufted into 10mm cut pile carpet.

- The durability of the treatment to shampooing was determined using three shampoo cycles according to the protocol outlined in IWS Test Method 28. A 45°C, 10g/l solution of non-ionic detergent was applied to the carpet using a spray/vacuum cleaner (Kerrick Hydra-Vac). The spray head was moved over the carpet at a speed of 3cm/sec. A second pass was made with vacuum only. The sample was dried at room temperature before the second and third respective cleaning cycles. The amount of permethrin removed was determined using an established HPLC assay technique. The treatment was found to be 94% fast to the shampoo treatment.

- The resistance of the carpet to insect attack was determined by using protocol of IWS Test Method 25. The test species used was Tineola

bisselliella. 15 larvae of equal size were placed on carpet discs (40mm diameter) in mesh-topped aluminium containers in a controlled environment for fourteen days. Four replicates were used. At the completion of the test the larvae mortalities were determined and carpet damage and weight loss assessed.

- 100% mortality and low mass losses/damage scores were achieved on all samples, giving a pass result to Wools of New Zealand (WNZ) Test Method 25 protocol.

- The above carpet was winch dyed using the following programme:

Auxiliaries:	0.2 g/l ALBEGAL FFD	(Ciba Geigy)
	1.5 g/l Sodium acetate	(BDH)
	1.25 ml/l Acetic acid	(BDH)
	1% omw Albegal SET	(Ciba Geigy)
	5% omw Sodium Sulphate	(BDH)
Dyes:	0.021% omw Lanaset Yellow 2R	(Ciba Geigy)
	0.018% omw Lanaset Blue 2R	(Ciba Geigy)
	0.077% omw Lanaset Red 2B	(Ciba Geigy)

- Raise bath temperature to 40°C - add auxilliaries
  - circulate 10 mins
  - add dyes
- Heat to 85°C @ 1°/minute
- Hold 30 minutes

- Dump bath, rinse
- Hydro extract
- The overall treatment level was 83% fast to this dyeing.

Example 2

Low-melt bi-component fibre was treated as in Example 1. This loose fibre was tested for treatment fastness to a simulated tape-scour train as follows:

Tape-scouring

Fibre was passed through a series of scour bowls with a roller-squeeze between each one.

Bowl (1) contained 1.5 g/l Teric GN9 (ICI) @ 65°C

Bowls (2), (3) and (4) were clean water rinses @ 65°C

There was 25 second immersion in each bowl followed by a squeeze to hydro-extract the fibre.

- The treatment level was 92% fast to this wet process.

Example 3

Low-melt bi-component PES fibre was treated as in Example 1.

This fibre was subjected to a simulated loose-stock dyeing to test for fastness.

Dye bath contained - 0.5% Albegal FFA (Ciba Geigy) omw

- 1.25 ml/l Acetic acid (BDH)
- 0.25% Avolan S (Bayer) (omw)

- Auxilliaries added to bath @ 50°C
- Fibre added to bath and temperature increased to 95°C @ 1°C/hour
- Hold at 95°C for 15 minutes
- Drop a cold rinse
- Fastness to this process was 75%.

Example 4

The low-melt sheath which constitutes about 50% of a bi-component fibre was doped in the melt with 3% permethrin prior to extrusion to produce an insect-resist fibre for blending with wool containing around 1.5% permethrin.

The treated fibre was subsequently blended with wool in the ratio 5%/95% PES/wool as in Example 1 and a similar bioassay carried out to give a pass result in terms of WNZ Test Method 25.

Example 5

Permethrin was added to low-melt polyester fibre at a rate of 1.5% on mass of polymer. The polymer chips were subsequently fed into a hopper, melted then extruded as an homogenous fibre containing about 1.5% insecticide. This was subsequently blended with wool in the ratio 95% wool/5% synthetic as for Example 1. The same level of protection is achieved.

Advantages of the invention are:

1. It eliminates the need to directly insect-proof the wool fibre;

2. It protects wool by incorporating a small proportion of a blend with doped synthetic fibre;

3. It provides a method for treating bi-component fibres with an insect-resist treatment which is substantially fast to subsequent wet processing and cleaning;

4. It provides a method of insect-proofing wool yarns, carpet, textiles, insulation materials or other woollen materials;

5. It provides a method of doping synthetic bi-component or low-melt fibres by exhaust methods;

6. It provides a method of protecting wool products by blending with synthetic fibres doped with pesticide prior to extrusion;

7. It provides a batchwise treatment which does not require effluent discharge between treatments; and

8. It provides a method of insect-proofing wool fibres with little subsequent loss of insect-resist agent during downstream wet processing of dyeing, tape-scouring and chemical setting.

Particular examples of the invention have been described and it is envisaged that modifications and variations can take place without departing from the scope of the appended claims.

CLAIMS

1. A method for insect-resist treatment of carpets, textiles and insulation products including the steps of pre-treating synthetic or regenerated natural fibres with an effective insecticide; and blending a proportion of the synthetic or regenerated natural fibre with wool fibres.

2. A method as claimed in claim 1 wherein the synthetic or regenerated natural fibre is pre-treated with the effective insecticide permethrin.

3. A method as claimed in claim 1 wherein the synthetic or regenerated natural fibre is pre-treated with an insect growth regulator or any compound having an insect-resist effect.

4. A method as claimed in claim 3 wherein the insect growth compound is RH5992 (Rohm & Hass), Abamectin, Lufenuron (Ciba Geigy), Bifenthrin (FMC Corporation), MGK 264 or a perfluoroalkylsulphonate (3M).

5. A method as claimed in any one of the preceding claims wherein the proportion of syntethic or regenerated fibres in the blend is $<5\%$ synthetic fibre of overall weight of wool.

6. A method as claimed in claim 1 and substantially as hereinbefore described with reference to any one of the Examples.

7. An insect-resist treated carpet, textile or insulation product manufactured in accordance with the method as claimed in claim 1.

8. An insect-resist treated carpet, textile or insulation product substantially as hereinbefore described.

AMENDED CLAIMS

[received by the International Bureau on 17 November 1997 (17.11.97); original claim 1 amended; remaining claims unchanged (1 page)]

1. A method of protecting wool and other animal fibres from being eaten by insect larvae by pre-treating synthetic or regenerated cellulose fibres with an effective insecticide and blending a small proportion of this pre-treated fibre with a larger proportion of untreated wool or other animal fibre.

2. A method as claimed in claim 1 wherein the synthetic or regenerated natural fibre is pre-treated with the effective insecticide permethrin.

3. A method as claimed in claim 1 wherein the synthetic or regenerated natural fibre is pre-treated with an insect growth regulator or any compound having an insect-resist effect.

4. A method as claimed in claim 3 wherein the insect growth compound is RH5992 (Rohm & Hass), Abamectin, Lufenuron (Ciba Geigy), Bifenthrin (FMC Corporation), MGK 264 or a perfluoroalkylsulphonate (3M).

5. A method as claimed in any one of the preceding claims wherein the proportion of syntethic or regenerated fibres in the blend is $<5\%$ synthetic fibre of overall weight of wool.

6. A method as claimed in claim 1 and substantially as hereinbefore described with reference to any one of the Examples.

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/NZ 97/00094

A. CLASSIFICATION OF SUBJECT MATTER

Int Cl[6]: D06M 13/236, 13/203, 13/222 // 101:32; A01N 25/10, 25/34

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC : D06M A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
WPAT : D06M AND PEST:, INSECT: A01N 25/-, 17/-, TEXTIL:, FIB:, CARPET:, INSULAT:

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Derwent Abstract Accession No 92-020381/03, Class A94, C03, D22, F06 (A14, A60), JP 03-269166 A (KANEBO KK) 29 November 1991 abstract	1, 2
X	Derwent Abstract Accession No 89-090019/12, Class A23, C03, D22, F06 (A35, A94), JP 01-040622 A (TEISAN SEIYAKU KK) 10 February 1989 abstract	1, 2
A	WO 91/19038 A (LAPPAGE) 12 December 1991 whole document	1-8

[X] Further documents are listed in the continuation of Box C

[X] See patent family annex

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search
19 September 1997

Date of mailing of the international search report
25 SEP 1997

Name and mailing address of the ISA/AU
AUSTRALIAN INDUSTRIAL PROPERTY ORGANISATION
PO BOX 200
WODEN ACT 2606
AUSTRALIA Facsimile No.: (02) 6285 3929

Authorized officer
GAYE HOROBIN
Telephone No.: (02) 6283 2069

INTERNATIONAL SEARCH REPORT

...ternational Application No.
PCT/NZ 97/00094

C (Continuation) **DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	AU 40848/85 B (578087) (CIBA-GEIGY) 10 October 1985 whole document	1-8

INTERNATIONAL SEARCH REPORT
Information on patent family members

International Application No.
PCT/NZ 97/00094

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
WO	9119038	AU	79890/91	NZ	233919		
AU	8540848	AU	578087	DE	3565562	EP	170611
		HK	344/91	JP	60231865	NZ	211697
		SG	321/91				

END OF ANNEX